

Electronic structure and magnetic and optical properties of double perovskite $\text{Bi}_2\text{FeCrO}_6$ from first-principles investigation

Zhe-Wen Song^{1,2} and Bang-Gui Liu¹

1. Beijing National Laboratory for Condensed Matter Physics,
Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

2. Department of Physics, Peking University, Beijing 100871, China

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Double perovskite $\text{Bi}_2\text{FeCrO}_6$, related with BiFeO_3 , is very interesting because strong ferroelectricity and high magnetic Curie temperature beyond room temperature are observed in it. However, existing density-functional-theory (DFT) studies, using pseudo-potentials, produce metallic ground state under the local density approximation (LDA) and need LDA+U method to yield needed non-metallic ground state, resulting in low magnetic Curie temperature (below 130 K). Here, we optimize its crystal structure and then investigate its electronic structure and magnetic and optical properties by combining the full-potential augmented plane wave method with Monte Carlo simulation. Our optimized structure is a robust ferrimagnetic semiconductor. This nonmetallic phase is formed due to crystal field splitting and spin exchange splitting, in contrast to Mott-Hubbard states in previous DFT studies. Spin exchange constants and optical properties are calculated. Our *ab initio* magnetic Curie temperature is 450 K, much higher than previous DFT-based value and consistent with experimental results. Our study and analysis reveals that the main magnetic mechanism is an antiferromagnetic superexchange between Fe and Cr over the intermediate O atom. These results are useful to understanding such perovskite materials and exploring their potential applications.

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I. INTRODUCTION

Magnetic materials keeping high spin polarization at room temperature or higher are highly desirable for spintronic applications^{1,2}. Half-metallic materials³ and ferromagnetic (or ferrimagnetic) semiconductors are intensively studied for this purpose. Up to 96% spin polarization has been achieved experimentally in the cases of (La,Sr) MnO_3 and CrO_2 materials^{2,4}. Since 1998, double perovskite oxides have been extensively explored. Both half-metals and semiconductors with macroscopic magnetization beyond room temperature have been found in such materials⁵⁻⁹. High quality samples of semiconductor technology standard have been achieved for some of these compounds¹⁰. Furthermore, it has been established that ferroelectricity and magnetism can coexist above room temperature in BiFeO_3 materials¹¹⁻¹³. These stimulate world-wide interest in exploring multiferroic materials for novel devices¹¹⁻¹⁴.

Double perovskite $\text{Bi}_2\text{FeCrO}_6$ can be constructed from BiFeO_3 , and is first predicted to have both ferroelectricity and ferrimagnetism, with theoretical electric polarization $80 \mu\text{C}/\text{cm}^2$ and magnetic Curie temperature below 130 K^{15,16}. Unfortunately, the Mott-Hubbard ground state excludes higher Curie temperature in such theoretical studies. Subsequently, the $\text{Bi}_2\text{FeCrO}_6$ is synthesized successfully by several groups, and experimental measurements on good samples reveal electric polarization up to $60 \mu\text{C}/\text{cm}^2$ and magnetic Curie temperature well above room temperature¹⁷⁻²³. The best experimental Curie temperatures are much higher than the first-principles predicted one, while the electric polarization is consistent between theory and experiment. Reason-

able explanation of this contradiction is highly desirable to understanding the basic physics of such materials and exploring their applications.

In this paper, we combine a full-potential density-functional-theory (DFT) method with Monte Carlo simulation to investigate double perovskite $\text{Bi}_2\text{FeCrO}_6$, with emphasis on its electronic structure and magnetic Curie temperature. We shall first optimize its structure with GGA and then study its electronic structure. We shall show that the resultant ferrimagnetic semiconductor phase is robust against both change of exchange-correlation potential and variation of structural parameters. Furthermore, we shall calculate spin exchange constants and thereby determine the magnetic Curie temperature. Our *ab initio* magnetic Curie temperature is 450 K, much higher than previous DFT-based value but consistent with experimental results. In addition, we shall present calculated optical properties. The magnetic mechanism is understood in terms of the electronic properties. More detailed results will be presented in the following.

The rest of this paper will be organized as follows. In the next section, we shall describe our computational details. In the third section we shall describe first-principles structural optimization and present our optimized results. In the fourth section we shall present main first-principles electronic structures. In the fifth section we shall present first-principles magnetic calculations and resulting Curie temperature. In the sixth section we shall present first-principles optical properties. In the seventh section we shall make some necessary discussions. Finally, we shall give our conclusion in the eighth section.

II. COMPUTATIONAL DETAILS

We use the full-potential augmented plane wave method within the density functional theory (DFT)²⁴, as implemented in package WIEN2k²⁵. Generalized gradient approximation (GGA)²⁶ is used for the exchange-correlation potential for calculating our main results, and local density approximation (LDA)²⁷ and a modified Becke-Johnson exchange potential (mBJ)²⁸ are also used for comparative calculations. Full relativistic effects are calculated with the Dirac equations for core states, and the scalar relativistic approximation is used for the other states²⁹⁻³¹. The spin-orbit coupling is neglected because it has little effect on our main conclusion (to be detailed in the following). The muffin-tin radii of Bi, Fe, Cr, and O are set to 2.13, 1.84, 1.84, and 1.64 bohr. The spherical expansion in the muffin-tin spheres is done up to $l_{max}=10$. The parameter $R_{mt} \times K_{max}$ is set to 7.5. We use 1500 k-points in the first Brillouin zone (226 k-points in the irreducible Brillouin zone) during the calculations. The self-consistent calculations are considered to be converged only when the integration of absolute charge-density difference per formula unit between the successive loops is less than $0.0001|e|$, where e is the electron charge.

Metropolis algorithm and variants are used for our Monte Carlo simulations^{32,33}. Several three-dimensional lattices of up to $30 \times 30 \times 30$ NaCl unit cells with periodic boundary condition are used in these calculations. The first 50,000 Monte Carlo steps (MCS) of total 100,000 MCS are used for the thermal equilibrium, and the remaining 50,000 MCS are used for a given temperature. The T_c value is determined through investigating the average magnetization and magnetic susceptibility as functions of temperature³³.

III. STRUCTURAL OPTIMIZATION

It has already been proved^{15,16} that the lowest energy structure of double perovskite $\text{Bi}_2\text{FeCrO}_6$ has R3 symmetry (space group # 146). Its structural difference from the cubic double perovskite is mainly due to the alternating rotations of oxygen octahedra around Fe/Cr cations. The magnetic order turns out to be ferrimagnetic with every Cr spin orienting upward and every Fe spin downward. We use experimental lattice constant $a = 5.537$ Å and $c = 13.502$ Å ($\alpha = 60.20^\circ$) which are intermediate values of existing experimental results¹⁷⁻²³. After internal structure optimization, every atom has a displacement from that of the cubic perovskite structure. We show its crystal structure in Fig. 1. The optimized parameters are summarized in Table I. The bond lengths and Fe-O-Cr bond angle can be calculated from the structural parameters. The calculated values are summarized in Table II.

These structural parameters are not much different from the previous LDA-optimized results^{15,16}. Actually,

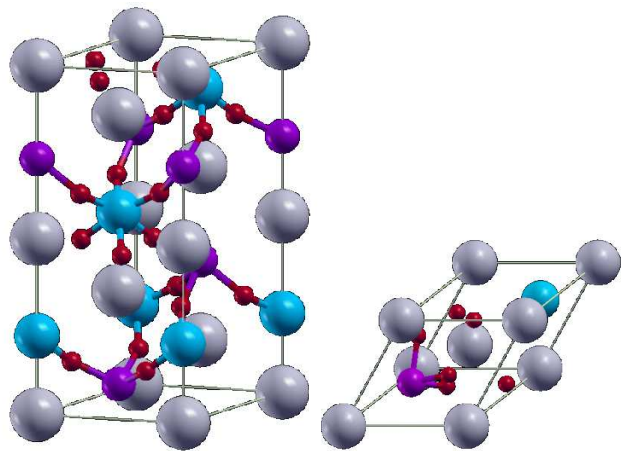


FIG. 1: (color online) The Rc (#146) Crystal structure of double perovskite $\text{Bi}_2\text{FeCrO}_6$. The right-side is the primitive cell, and the left-side is used to describe the relative positions of the atoms. O, Fe, Cr, and Bi are denoted by colorful balls with different size from the smallest to the biggest.

TABLE I: Optimized internal structural parameters of double perovskite $\text{Bi}_2\text{FeCrO}_6$ with the Rc (#146) crystal structure.

Atom	Parameter	Values
Bi	z_1	0.0005, 0.5040
Fe/Cr	z_2	0.7330/0.2260
O	x	0.5433, 0.0511
	y	0.9542, 0.9043
	z	0.3937, 0.4459

we obtain $55.2 \mu\text{C}/\text{cm}^2$ for the sum $\sum_i z_i u_i$ of formal charge z_i times displacement u_i , using formal charges 3.0, 3.0, 3.0, and -2.0 for Bi, Fe, Cr, and O, respectively. This value is almost the same as the previous $55 \mu\text{C}/\text{cm}^2$ in Refs. 15 and 16. Therefore, we believe that similar ferroelectric polarization can be calculated with the present structural parameters. The total magnetic moment is equivalent to $2\mu_B$ per formula unit. Different magnetic moments, $3.70\mu_B$ and $2.18\mu_B$, are observed in the spheres of Fe and Cr atoms, and magnetic moments in the spheres of other atoms are tiny. These implies that Fe and Cr are both in the high spin states.

TABLE II: Bond lengths (Å) and Fe-O-Cr angle ($^\circ$) of double perovskite $\text{Bi}_2\text{FeCrO}_6$ with the Rc (#146) crystal structure.

Bond length	Fe-O	2.130, 1.971
	Cr-O	1.947, 1.994
	Bi-O	2.347, 2.387
		2.406, 2.416
Bond angle	Fe-O-Cr	153.7, 153.6

IV. ELECTRONIC STRUCTURE

With the optimized crystal structure, we can study the electronic structure of the $\text{Bi}_2\text{FeCrO}_6$. In Fig. 2 we present the spin-resolved total density of states (DOS) and partial DOS projected in the d states of Fe and Cr between -7.3 and 5 eV. The corresponding spin-dependent band structure is presented in Fig. 3. It is clear that the $\text{Bi}_2\text{FeCrO}_6$ is a ferrimagnetic semiconductor, in contrast with the ferrimagnetic metallic phase obtained in previous pseudo-potential calculations^{15,16,34,35}.

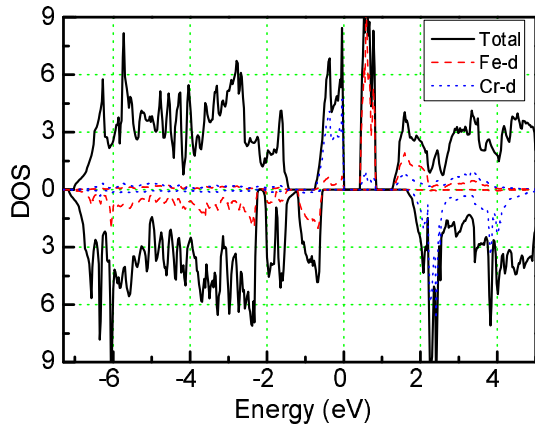


FIG. 2: (color online) Spin-resolved density of states (DOS, in state/eV per formula unit) of double perovskite $\text{Bi}_2\text{FeCrO}_6$, calculated with GGA. The solid line is total DOS, and dashed and dotted lines refer to partial DOS projected in the atomic spheres of Fe and Cr, respectively. The upper part in each panel is majority-spin DOS result, and the lower the minority-spin one.

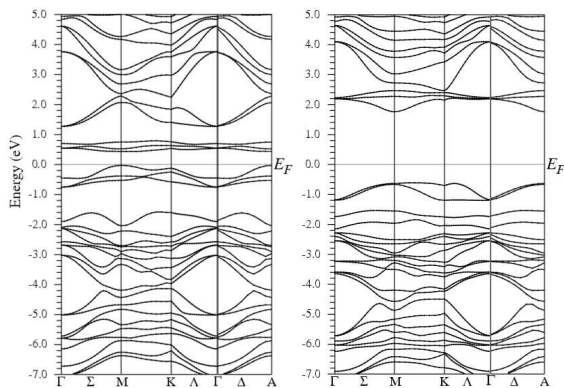


FIG. 3: (color online) Spin-resolved energy bands of double perovskite $\text{Bi}_2\text{FeCrO}_6$, calculated with GGA. The left-side panel is for majority-spin, and the right-side for minority-spin.

In the majority-spin channel, the bands between -7.3 and -1.4 eV are from the 18 O 2p states; the three bands between -0.8 and 0 eV originate mainly from Cr 3d t_{2g}; the three empty bands are almost Fe 3d t_{2g} states; and the upper states are from Fe 3d eg, Cr 3d eg, and Bi

6p. In the minority-spin channel, the 23 filled bands are from 18 O 2p states and 5 Fe 3d ones; and the empty bands from Cr 3d and Bi 6p states. Here, the Fe 3d states hybridize with the O 2p and the Cr 3d ones interact strongly with the Bi 6p, in contrast to the majority-spin channel.

Because it is well known that both LDA and GGA underestimate semiconductor gap, we use a new exchange potential, mBJ, to improve the electronic structure, especially the semiconductor gap. The mBJ DOS are presented in Fig. 4. The main features are similar to the GGA results, except that the mBJ gap is much wider than the LDA and GGA ones. The three semiconductor gaps are summarized in Table III.

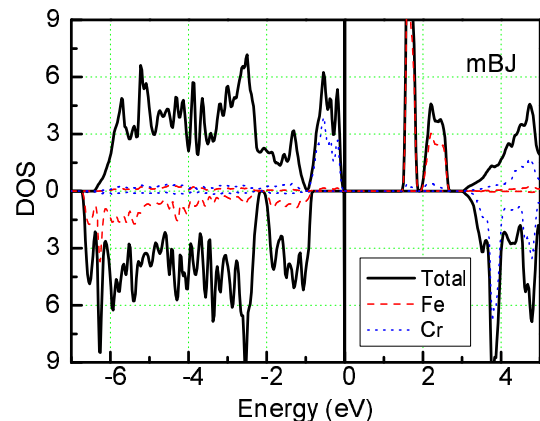


FIG. 4: (color online) Spin-resolved density of states (DOS, in state/eV per formula unit) of double perovskite $\text{Bi}_2\text{FeCrO}_6$, calculated with mBJ. The solid line is total DOS, and dashed and dotted lines refer to partial DOS projected in the atomic spheres of Fe and Cr, respectively. The upper part in each panel is majority-spin DOS result, and the lower the minority-spin one.

TABLE III: The semiconductor energy gaps (in eV) of double perovskite $\text{Bi}_2\text{FeCrO}_6$, calculated with our optimized structure and previous one^{15,16} in terms of LDA, GGA, and mBJ.

Structure	LDA	GGA	mBJ
this	0.26	0.42	1.48
previous ^{15,16}	0.30	0.48	

Our study shows that this feature of ferrimagnetic semiconductor is robust to a changing of crystal structure parameters. For example, the GGA and LDA gaps in the lower line of Table III are calculated with the previous structure parameters^{15,16}.

V. MAGNETIC CURIE TEMPERATURE

In order to study spin exchange interactions, we compare the total energies of the four magnetic configurations

in the supercell consisting of 20 atoms, namely ferrimagnetic (the ground state) and ferromagnetic orders, and two other magnetic orders constructed by reversing one of the two Cr or Fe spins in the ferrimagnetic order. With respect to the ground state, the three magnetic structures have total energies: 310, 161, and 166 meV per formula unit, respectively. Because the induced spin density at the other atoms are very small compared to those at the magnetic atoms, we consider only Fe and Cr. The magnetic energies reflect the spin exchange energies e_{ij} where i and j denote two different spins. Fe and Cr atoms form a lattice of the NaCl crystal structure^{5,7,8,17,20}. While the magnetic moments in the spheres of Fe and Cr are 3.70 and 2.18 μ_B , the Fe^{3+} and Cr^{3+} cations contribute 5 and 3 μ_B , respectively. We can assign spin values $s = \frac{5}{2}$ and $s = \frac{3}{2}$ to the Fe and Cr spins, respectively. Therefore, we obtain the effective spin Hamiltonian:

$$H = \sum_{\langle ij \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j \quad (1)$$

where \vec{S}_i is spin operator at site i (in both of the Fe and Cr sublattices), the summation is over spin pairs, and the spin exchange constant J_{ij} is limited to the nearest (Fe-Cr) and the next nearest (Fe-Fe and Cr-Cr) spin pairs. There exists a relation between the energies e_{ij} and constants J_{ij} , $e_{ij} = J_{ij} s_i s_j$, where s_i takes either $\frac{5}{2}$ or $\frac{3}{2}$. The spin exchange energies e_{ij} and constants J_{ij} are summarized in Table IV.

TABLE IV: The calculated spin exchange energies (e_{ij}) and constants (J_{ij}) of double perovskite $\text{Bi}_2\text{FeCrO}_6$ for the nearest and next nearest spin pairs ($\langle ij \rangle$), and the resulting Curie temperature T_c from Monte Carlo simulation.

$\langle ij \rangle$	Fe-Cr	Fe-Fe	Cr-Cr
e_{ij} (meV)	25.8	-1.88	-1.06
J_{ij} (meV)	6.89	-0.30	-0.47
T_c (K)	450		

We carry out Monte Carlo simulations of the Heisenberg model to estimate the T_c of the materials^{32,33}. It is well known that Curie temperature will be a little underestimated if classical approximation to the Heisenberg model is used in the Monte Carlo simulation. We use Monte Carlo simulation of the classical Heisenberg model to give a lower bound for the Curie temperature of the quantum spin model (1). Our simulated average magnetization (in unit of $2\mu_B$ per Fe-Cr pair) as a function of temperature from classical Heisenberg model is presented in Fig. 5. Because the classical approximation is used, the low-temperature part is not very accurate with respect to the model (1), but the high-temperature part should be accurate enough to get reasonable Curie temperature. The calculated T_c value is equivalent to 450 K, meaning that real Curie temperature should be a little higher than 450 K. This Curie temperature is

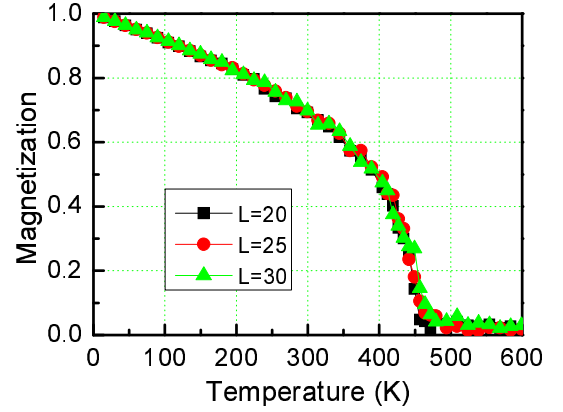


FIG. 5: (color online) Temperature dependent magnetization (in unit of $2\mu_B$ per Fe-Cr pair) of double perovskite $\text{Bi}_2\text{FeCrO}_6$, simulated with Monte Carlo method and the classical Heisenberg model.

much higher than the original prediction (lower than 130 K)^{15,16}, but it is consistent with experimental high Curie temperatures beyond room temperature^{17,20–23}.

VI. OPTICAL PROPERTIES

Because optical properties are important to semiconductor, we calculate the direct electronic contributions of the optical dielectric function $\epsilon(\omega)$ and optical conductivity $\sigma(\omega)$ curves of the $\text{Bi}_2\text{FeCrO}_6$ as functions of photon energy (ω). Considering that the semiconductor gaps have important impact on the low-energy parts of these optical functions, we calculate them with both GGA and mBJ. These results, both real (Re) and imaginary parts (Im) between 0 and 12 (or 13) eV, are presented in Figs. 6 and 7.

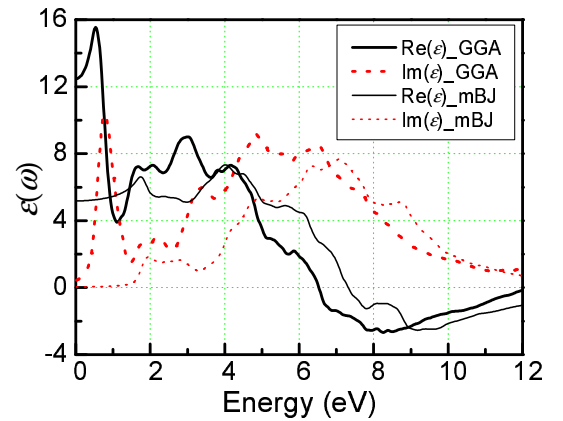


FIG. 6: (color online) Optical dielectric functions, both real (solid) and imaginary (dotted) parts, of double perovskite $\text{Bi}_2\text{FeCrO}_6$, calculated with GGA (thick) and mBJ (thin).

For $\text{Re}(\epsilon)$, the GGA result of the low energy limit is substantially larger than the mBJ one, both have simi-

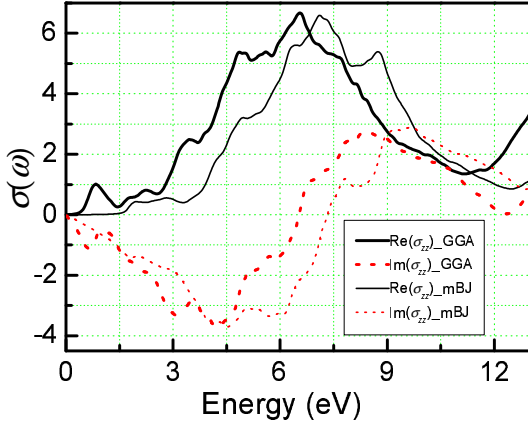


FIG. 7: (color online) Optical electric conductivity, both real (solid) and imaginary (dotted) parts, of double perovskite $\text{Bi}_2\text{FeCrO}_6$, calculated with GGA (thick) and mBJ (thin).

lar trend when the photon energy is larger than 1.5 eV. For $\text{Im}(\epsilon)$, main difference appears for low energy (0-1.5 eV). There is a sharp peak at 0.75 eV for the GGA result, which is related to the steep decrease in the GGA curve of $\text{Re}(\epsilon)$ at the same photon energy. The mBJ result of $\text{Im}(\epsilon)$ is equivalent to zero in this region, reflecting the broad semiconductor gap from mBJ. For higher energy, both of the results are similar. For the $\sigma(\omega)$ curves, the main difference also appears in the low energy region, $\text{Re}(\sigma(\omega))$ having a peak approximately at 1.0 eV and $\text{Im}(\sigma(\omega))$ having a valley approximately at 0.5 eV. For the higher energy, both of the $\sigma(\omega)$ curves have similar behaviors. These calculated optical functions could be useful in exploring the optical properties of the $\text{Bi}_2\text{FeCrO}_6$ materials and others similar.

VII. DISCUSSIONS

Our DFT investigation with GGA, LDA, and mBJ shows that the ground-state phase of double perovskite $\text{Bi}_2\text{FeCrO}_6$ is a ferrimagnetic semiconductor with a clear semiconductor gap (larger than 0.26 eV), in contrast to previous ferrimagnetic metallic phases from LDA pseudopotential calculations^{15,16,34,35}. Even using the previous structural parameters^{15,16}, we still obtain the ferrimagnetic semiconductor phase with both GGA and LDA. Furthermore, our spin exchange energies and interaction constants produce the high Curie temperature 450 K which is consistent with experimental high Curie temperature beyond room temperature^{17,20-23}. This is in contrast to the previous LDA+U calculations which yield Mott-Hubbard insulator phases and low Curie temperatures (below 130 K)^{15,16}. These imply that we need not use LDA+U or GGA+U to achieve the reasonable ferrimagnetic semiconductor phase for double perovskite $\text{Bi}_2\text{FeCrO}_6$.

Here, our semiconductor gap is formed between the

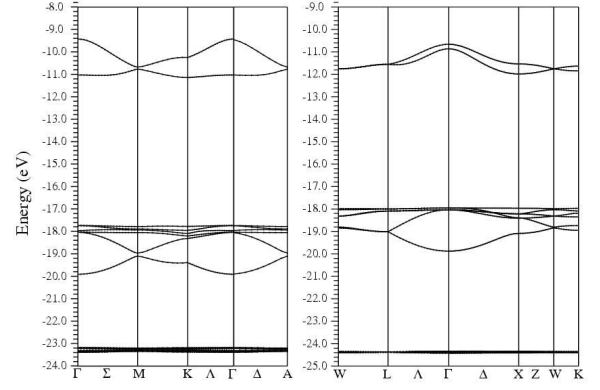


FIG. 8: (color online) The majority-spin part of the Bi 6s, O 2s, and Bi 5d energy bands of double perovskite $\text{Bi}_2\text{FeCrO}_6$ in the R3 (the left part) and cubic (the right part) structures, calculated with GGA.

filled Cr 3d t_{2g} and the empty Fe 3d t_{2g} bands. Essentially, it is originated mainly from the crystal field splitting due to the deformation of the O octahedrons plus the spin exchange splitting of the 3d electrons. Our calculated spin exchange interaction between the nearest Fe and Cr atoms is positive, and the next nearest (Fe-Fe and Cr-Cr) ones are negative. These spin interactions become substantially weaker from the nearest to next nearest neighboring spin pairs, which implies that such a spin description is reliable. The main spin interaction is intermediated by the O atom in between the nearest Fe and Cr atoms. The Fe and Cr spins contribute opposite magnetic moments so that the ferrimagnetism is formed. Therefore, the main magnetic mechanism is the antiferromagnetic superexchange over the O atom.

Now we address possible contributions from deeper energy levels. For this purpose, we present in Fig. 8 the bands of Bi 6s, O 2s, and Bi 5d states of the R3 (space group #146) and cubic (space group #225) structures. They are below -9 eV from the Fermi levels. The Bi 5d bands (-23.3 or -24.4 eV) in both of the structures are completely flat, meaning that Bi 5d states are isolated, but there is a clear correlation between the two Bi 6s bands (from -11.0 to -9.4 eV) and two of the six O 2s ones (from -19.9 to -17.7 eV) in the case of the R3 structure. Noticeably, its Bi 6s bands are more separated from the O 2s ones than those of the cubic structure. This can be attributed to the expelling due to the small but nonzero hybridization of the two sets of s states. The interaction between the Bi 6s and O 2s states should be involved in the ferroelectric property in the R3 structure, because they are absent in the cubic structure without ferroelectricity.

VIII. CONCLUSION

In summary, we have investigated the electronic structure and magnetic and optical properties of double per-

ovskite $\text{Bi}_2\text{FeCrO}_6$ by combining the full-potential augmented plane wave method with Monte Carlo simulation. Our calculations show that our full-potential GGA-optimized phase is a ferrimagnetic semiconductor and it is robust against both change of exchange-correlation potential and variation of structural parameters. This non-metallic phase is formed due to crystal field splitting and spin exchange splitting, in contrast to Mott-Hubbard insulating state in previous DFT studies. Spin exchange constants and optical properties are calculated. Our *ab initio* magnetic Curie temperature is 450 K, much higher than previous DFT-based value but consistent with experimental results. Our study and analysis reveals that

the main magnetic mechanism is an antiferromagnetic superexchange between Fe and Cr over the intermediate O atom. Our results are useful to understanding such materials and exploring their potential applications.

Acknowledgments

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